

Low-Defect Carbon Nanotubes Supported Pt-Ni Alloy Nanoparticles for Direct Methanol Fuel Cells Applications

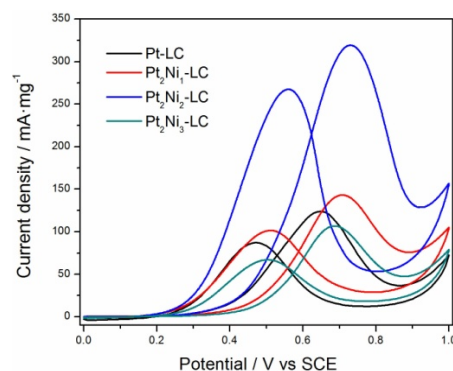
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The direct methanol fuel cells (DMFCs), which use methanol for fuel directly, have received considerable attention for applications in vehicle power supplies and portable electronic devices. Methanol as fuel has many advantages over pure hydrogen such as a liquid at ambient conditions, easy to stored and transported, low cost, high theoretical energy density, and low operating temperatures. As it is well-known, platinum has been traditionally the most active single metal for the electrocatalytic oxidation of methanol. However, pure platinum is high cost and susceptible to carbon monoxide poisoning at room or moderate temperature. Aiming to lower the cost of catalysts, augment methanol oxidation activity, and prevent poisoning, Pt-based bimetallic catalysts have been intensively studied in recent decades. Another common approach to improve the methanol oxidation activity is to deposit bimetallic catalysts onto carbon support. The carbon nanotubes (CNTs) have been the focus of attention, owing to their high specific surface, high electrical conductivity and unique structural properties among several carbon support materials.

It is extremely difficult to deposit metal directly onto the surface of CNTs due to the chemical inertness of CNTs. So the modification of CNTs is absolutely essential. And the approaches for the modification of CNTs may be roughly divided into two categories: covalent attachment functionalization and non-covalent absorption. The former method may reduce the electrical, mechanical, and optical properties of CNTs on account of a great deal of framework defects will be produced during the process. For the latter, the metal on the surface of CNTs can be easy drop out due to the weaker noncovalent interactions compared to covalent bonds. Therefore, it is essential to develop a mild and simple strategy for the formation of metal nanoparticles-CNTs catalysts with low defect and high electrocatalytic activity.

In our research, we successfully dispersed Pt-Ni alloy nanoparticles on low-defect CNTs (PtNi-LC) by in situ oxidation of CNTs by a mild, simple, controllable, soft chemistry method. We use  $H^+$  from hydrolysis of platinum nitrate and nickel nitrate to bring oxygen-containing groups onto the surface of CNTs, then the in situ formation of PtNi alloy nanoparticles on the CNTs surface can be accomplished in the presence of  $NaBH_4$ . As shown in Fig. 1, the electrocatalytic properties of Pt nanoparticles on low-defect CNTs (Pt-LC) and PtNi-LC with differing Pt:Ni feeding atomic ratios toward methanol oxidation reaction in acid medium were investigated using cyclic voltammetry. It can be clearly seen that the  $Pt_2Ni_2$ -LC catalyst exhibited the best electrocatalytic performance which is much higher than the Pt-LC catalyst according to the forward anodic peak current density among these samples.



**Fig.1** CVs of Pt-LC, Pt<sub>2</sub>Ni<sub>1</sub>-LC, Pt<sub>2</sub>Ni<sub>2</sub>-LC and Pt<sub>2</sub>Ni<sub>3</sub>-LC in 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M methanol solution.